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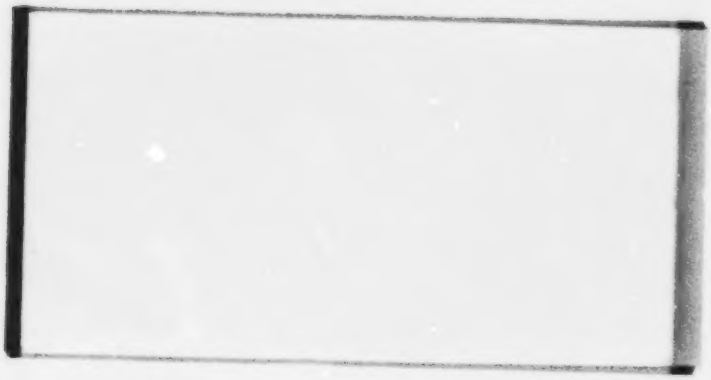

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PRECIPITATION SCAVENGING OF TRITIATED WATER VAPOUR (HTO)

Report No 85-233-K

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ABSTRACT

Precipitation scavenging (or washout) is an important mechanism for the removal of HTO from the atmosphere. Methods of parameterizing the depletion of a plume of HTO released to the atmosphere are examined. Simple approaches, commonly used for atmospheric transport modelling purposes, such as the use of a constant washout coefficient or washout ratio, or the use of parameters based on equilibrium assumptions, are often not justified. It is shown that these parameters depend strongly on ambient temperature and plume dimensions, as well as rainfall rate. An approximate expression for washout ratio, as a function of these variables, is developed, and it is shown that near equilibrium washout conditions are only expected to hold at long plume travel distances. A possible method of treating scavenging by snow is also suggested.

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EXECUTIVE SUMMARY

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Tritiated water vapour (HTO) is an important emission from CANDU systems. In order to mathematically model the fate and impact of HTO emitted to the atmosphere it is necessary to quantify the effect of atmospheric transport and removal processes. A removal process that is expected to be of particular importance for HTO is scavenging by precipitation (often referred to as washout).

The purpose of this report was to review and evaluate potential methods of parameterizing HTO washout with the objective of establishing simple but sufficiently realistic methods for modelling purposes. It was found that the commonly used assumption of equilibrium scavenging was a poor assumption for short travel distances. New expressions were therefore developed to describe the washout ratio (ratio of liquid phase to gas phase HTO concentration at ground level) and its departure from equilibrium values as a function of plume dimensions and temperature.

An estimate of the upper limit to the scavenging rate by snow was obtained by assuming an irreversible uptake process.

Recognizing that little data exists for testing and validating theoretical washout parameters, a series of simple field experiments to measure washout ratios using routine emissions, is recommended.

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To F.J. Kee
Director of Research

PRECIPITATION SCAVENGING OF TRITIATED WATER VAPOUR (HTO)

1.0 INTRODUCTION

Tritiated water vapour is a uniquely important emission, to the atmosphere, from CANDU reactor systems because of the use of heavy water as a moderator and heat transfer fluid (Ogram 1982, 1983). Tritium is formed by neutron activation of deuterium.

In order to predict the fate and impact of released HTO, by means of an atmospheric transport model, it is necessary to be able to quantify both the extent of depletion of the plume due to the action of precipitation scavenging, and the concentration of scavenged tritium in rainfall reaching the ground. This report examines methods of parameterizing HTO washout "with the objective of establishing simple but sufficiently realistic methods" for modelling purposes (Ogram and Melo 1984). The treatment is restricted to the case of precipitation forming above the plume, as illustrated in Figure 1, ie, the plume is taken to be below cloud level. Initially "uncontaminated" precipitation drops fall through the plume, where they absorb HTO from the atmosphere.

It will be shown that a relationship describing equilibrium between HTO concentrations in the gas and liquid phases can be derived. The characteristic time scales (and corresponding drop fall distances) required for a drop to equilibrate with the surrounding air are shown to depend on drop dimensions and ambient temperature and are compared to the corresponding residence times of the drop in the plume (Section 2).

Common methods of parameterizing the precipitation scavenging process, for modelling purposes, are then discussed (Sections 3 and 4). An expression developed by Hales (1972a) to describe the HTO concentration in a drop reaching ground level after falling through a Gaussian plume is used to derive the effective washout ratio as a function of plume vertical dimensions,

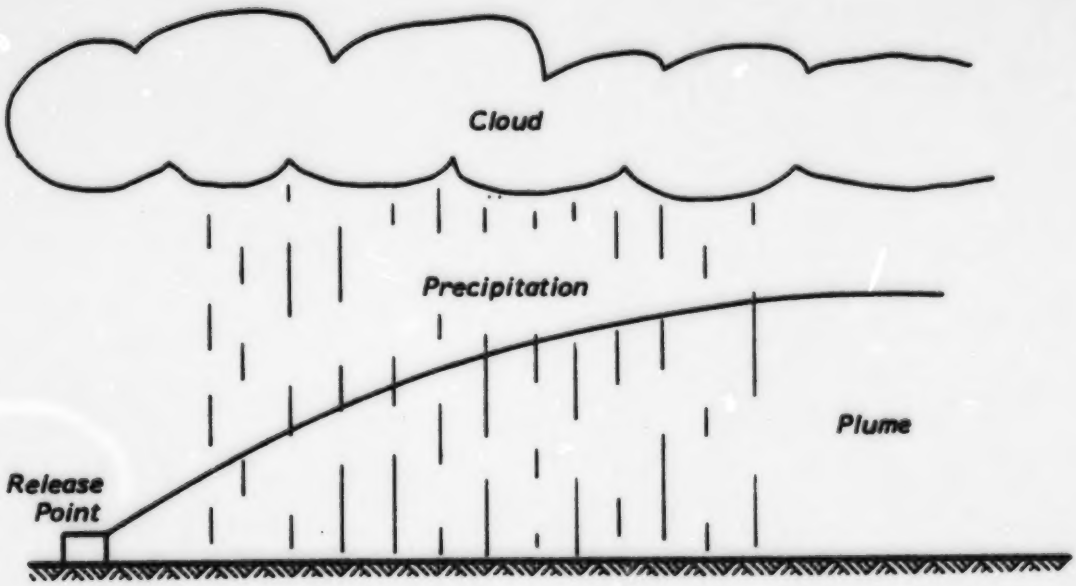

FIGURE 1

SCHEMATIC OF BELOW-CLOUD SCAVENGING OF A PLUME OF HTO

temperature and rainfall rate (Section 4). It is shown that the commonly used assumption of equilibrium scavenging may greatly overestimate plume depletion (Section 5).

Very little information is available regarding the scavenging of HTO by snow. An expression is derived using assumptions that should give an upper limit on scavenging rate (Section 6).

Finally it is pointed out that little experimental information exists regarding HTO scavenging. Theoretically derived scavenging rates should therefore be used with caution, except perhaps in the case of long enough travel distances for equilibrium scavenging conditions to hold.

Note that Sections 2 and 3 develop the technical framework necessary to understand the conclusions of this report. Readers wishing to proceed directly to the major results are referred to Section 4 (Equation (33) and Figure 4) and Section 6 (Equation (38) and Table V).

2.0 EQUILIBRIUM HTO CONCENTRATIONS

Consider the case of an initially uncontaminated drop falling through air containing HTO. Transport of tritium into the drop will occur until equilibrium is reached with the tritium remaining in the air. At equilibrium, by Raoults law, the partial pressure of HTO remaining in the air, P, should correspond to the product of the vapour pressure, P_{vap}, of HTO and the mole fraction, X, of HTO in the liquid, ie,

$$P = P_{vap}\, X \qquad (1)$$

where P and P_{vap} are usually expressed in atmospheres and X is dimensionless (Hales 1972a). Table I shows HTO vapour pressures at various temperatures. The vapour pressure of H_2O is shown for comparison. Because of the strong temperature dependence of vapour pressure the relative concentrations of HTO in the liquid and vapour phases will be highly temperature dependent.

If the relative humidity is 100%, then it follows that the equilibrium condition corresponds to having approximately equal specific activities (radioactivity per unit mass of water or water vapour) of HTO in the drop and in the water vapour in the surrounding air. That is

$$\frac{P_{HTO}}{P_{H_2O}} = \frac{X_{HTO}}{X_{H_2O}}$$

TABLE I

HTO Vapour Pressures and Equilibrium Ratios Between Liquid and Gas Phase HTO Concentrations, α

T(°C)	Vapour Pressure [a] (atm)		[b] α
	H_2O	HTO	
0	0.0060	0.0053	2.35×10^5
5	0.0086	0.0076	1.67×10^5
10	0.0121	0.0108	1.19×10^5
15	0.0168	0.0151	8.70×10^4
20	0.0231	0.0210	6.37×10^4
25	0.0313	0.0286	4.76×10^4
30	0.0419	0.0385	3.58×10^4

[a] from Hales (1972), based on data by Jones (1968) and Van Hook (1968).

[b] These dimensionless coefficients, α, represent equilibrium ratios of concentrations expressed as amount of HTO (B_q, Ci, g, molecules, moles, etc) per unit volume of liquid and air, respectively.

In fact, because of the isotopic effect on vapour pressure the specific activity in the drop will be slightly (~10%) higher (Table 1).

For practical purposes it is often more useful to use units of amount per unit volume (eg, moles m^{-3}, Ci m^{-3}, g cm^{-3}, Bq m^{-3} etc) to describe concentrations in the liquid and gas phases. The partial pressure of HTO may be related to the gas phase concentration, c_g, by the ideal gas law. The liquid phase HTO concentration, c_l, may be determined simply from the mole fraction, X, if $X \ll 1$, as will certainly be the case in treating HTO released to the atmosphere from nuclear power activities. The equilibrium ratio of c_l to c_g can then be derived, and depends on temperature alone, ie

$$c_l = \alpha\,(T)\, c_g \qquad (2)$$

where the coefficient α is given in terms of the vapour pressure of HTO as

$$\alpha = \frac{R'T}{P_{vap}} \frac{\rho_{H_2O}}{M_{H_2O}} \qquad (3)$$

where R' is the universal gas constant (82.05 atm cm^3 K^{-1}), T is temperature (K), P_{vap} is the vapour pressure of HTO (atm), ρ_{H_2O} is the density of water ($\approx$1 g cm^{-3}) and M_{H_2O} is the molecular weight of water ($\approx$18 g $mole^{-1}$). The values of α given in Table I apply for any consistent set of units (for example c_g expressed in Ci cm^{-3} of air, and c_l in Ci cm^{-3} of liquid). Note that (2) is similar to the definition of solubility coefficient for gases that form ideal solutions (Slinn 1984). Therefore α may be conveniently thought of as an effective solubility coefficient for HTO. The treatment that follows for HTO can be equally well applied to the scavenging of any gas for which a solubility coefficient, or effective solubility coefficient, can be defined by a relationship like (2).

2.1 Drop Equilibrium Times

The rate at which a drop, falling through a contaminated atmosphere, reaches equilibrium, with the gas phase concentration, is examined here. Consider an initially uncontaminated drop of diameter D falling through air containing HTO at a concentration c_g. For drops of the size of falling rain drops it is justified to assume that uptake of HTO is limited by gas phase transfer only, as frictional forces set up convection patterns which rapidly mix the material, absorbed at the drop surface, into the drop (Slinn 1984). An expression may therefore be derived for the rate of change of drop HTO concentration with time in the following way.

The flux of HTO to the drop (amount of HTO reaching the drop, per unit time, per unit area) can be written as

$$F = k_g (c_g - c_l/\alpha) \qquad (4)$$

That is, the flux is proportional to the difference between the actual gas phase concentration and the gas phase concentration that would be in equilibrium with the drop concentration (Hales 1972a, b, Slinn 1984).

k_g is a mass transfer velocity which may be approximated by the semi-empirical Frossling (1938) relation

$$k_g = \frac{D_g}{D} [2 + 0.60\ Re^{1/2} Sc^{1/3}] \quad (5)$$

where D_g is the gas phase diffusion coefficient for HTO, $Re = Dv_z/\nu$ is the Reynolds number (where v_z is the drop terminal fall velocity and ν is the kinematic viscosity of air) and $Sc = \nu/D_g$ is the Schmidt number. This expression has been shown to be in good agreement with experimental studies (Pruppacher and Klett 1980).

The rate of change of concentration in a drop of surface area A and volume V is related to the flux of material to the drop by

$$\frac{dc_\ell}{dt} = F \cdot A/V \quad (6)$$

which on using (4) and (5) becomes

$$\frac{dc_\ell}{dt} = \frac{6\ k_g}{D} \left(c_g - \frac{c_\ell}{\alpha}\right) \quad (7)$$

If c_g is held constant, (7) has the solution.*

$$\left[c_g - \frac{c_\ell}{\alpha}(t)\right] = e^{-t/\tau} \left[c_g - \frac{c_\ell}{\alpha}(t=0)\right] \quad (8)$$

where τ, the characteristic relaxation time with which equilibrium is approached, is given by

$$\tau(T,D) = \alpha D/6\ k_g \quad (9)$$

Note that τ depends on drop diameter and temperature T (through α).

If the initial drop concentration, $c_\ell(t=0)$, is zero, (initially uncontaminated drop), then (8) can be written as

$$c_\ell(t) = \alpha\ c_g\ (1 - e^{-t/\tau}) \quad (10)$$

where $\alpha\ c_g$ corresponds to the equilibrium drop concentration attained at large times.

---

*The solution to (7), with c_g having a Gaussian vertical profile, is given in Section 4.0.

For a drop falling at terminal velocity, v_z, a relaxation or equilibration distance z_e can be defined as

$$z_e = v_z \tau$$

Figures 2 and 3 show values of τ and z_e calculated, for various temperatures, as a function of drop diameter. The data given in Tables I and II were used as input.

The diffusion coefficient, D_g, for HTO in air was estimated from D_g for H_2O in air (Pruppacher and Klett, 1980) by assuming D_g inversely proportional to the square root of molecular weight.

Note that equilibrium is much more rapidly achieved at higher temperatures, because the equilibrium amount of HTO in the liquid phase increases with decreasing temperature. At lower temperatures more HTO must be transported to the drop to reach equilibrium, hence the increased equilibration time.

Laboratory experiments on the rate of exchange of HDO and HTO between a drop and the surrounding air gave equilibration rates which were in good agreement with (9) (Friedmann et al 1962, Booker 1965).

TABLE II

Parameters used in calculation of drop relaxation times.

Quantity	Symbol	Formula
Gas phase diffusion coefficient of HTO	D_g	$D_g(HTO) = (\frac{18}{20})^{0.5} D_g(H_2O)$ $= 0.20 (\frac{T}{273.15})^{1.94} (\frac{1013.25}{P})_{cm^2 s^{-1}}$ where P is in mbar and T in K.
Kinematic viscosity of air	ν	$\nu = 0.1177 (\frac{T}{273.15})^{1.79}_{cm^2 s^{-1}}$ (Fenton et al 1980)
Drop fall velocity	v_z	$1300\ D^{1/2}$ cm s^{-1} where D is in cm (Kessler 1969)

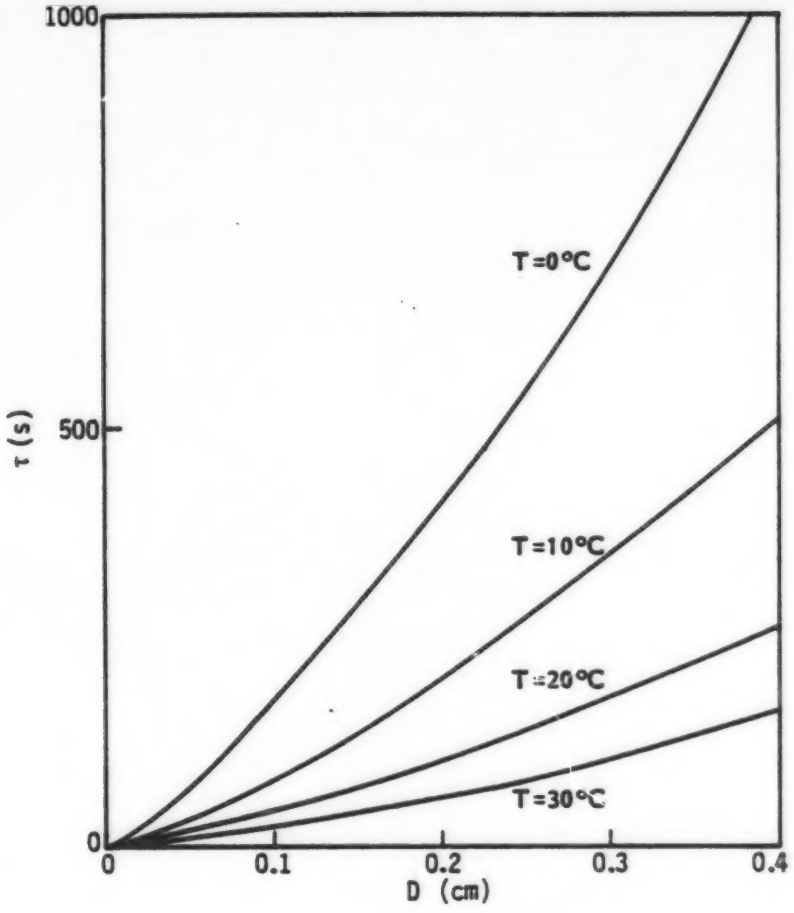

FIGURE 2

DROP EQUILIBRIUM TIME PLOTTED AGAINST DROP DIAMETER FOR VARIOUS TEMPERATURES

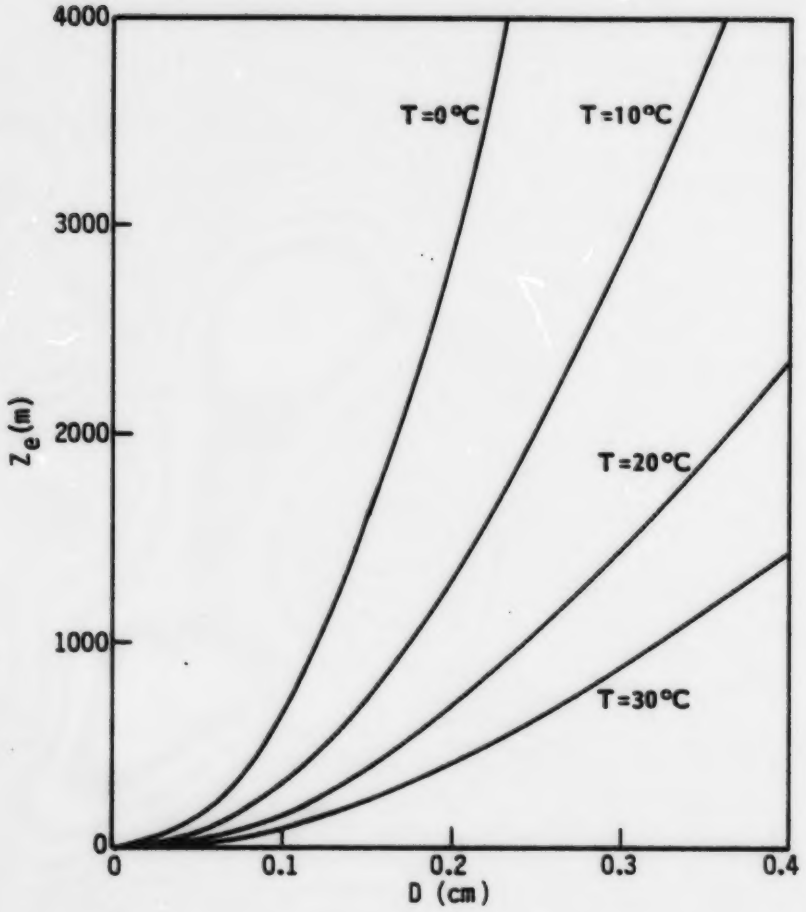

FIGURE 3

DROP EQUILIBRATION DISTANCE PLOTTED AGAINST DROP DIAMETER FOR VARIOUS TEMPERATURES

We can use the data of Figures 2 and 3 to examine whether rain drops of typical size are likely to reach equilibrium with an HTO plume of given vertical extent.

To obtain an idea of typical drop sizes the commonly used Marshall-Palmer distribution may be introduced (Pruppacher and Klett, 1978), whereby the number of drops per unit volume of air per unit increment in drop diameter is

$$n(D) = 0.08 \exp [-41\ R^{-0.21} D]\ cm^{-4} \qquad (11)$$

where R is the rainfall rate (mm h^{-1}).

The mean droplet mass is

$$\overline{M} = \int_0^\infty n(D)\ (\frac{\pi D^3}{6}\rho)dD\ /\ \int_0^\infty n(D)\ dD \qquad (12)$$

where ρ is the density of water.

A representative drop size is given by the mass mean diameter, D_m, defined as follows.

$$\overline{M} = \frac{\pi}{6}\ \rho\ \overline{D^3} = \frac{\pi}{6}\ \rho\ D_m^3 \qquad (13)$$

Equations (11), (12) and (13) give.

$$D_m = 0.044\ R^{0.21}\ cm \qquad (14)$$

Values of D_m for R ranging from light to very heavy rainfall are given in Table III. These values, when compared to Figure 3, indicate that above 10°C most drops would equilibrate within a few hundred meters fall distance. Conversely, for the case where the plume height is significantly less than a few hundred meters, significant departures from equilibrium may be expected in drops reaching the ground.

TABLE III

Mass mean drop diameters for various rainfall rates.

R(mm h^{-1})	1	2.5	5	10	25
$\overline{D}_m$(cm)	0.044	0.054	0.062	0.072	0.087

The above argument was carried out by averaging over the drop size distribution. However, because heavier drops fall more rapidly, they contribute to the net rainfall to a greater degree. If the above size distribution is transformed to describe the size distribution of drops reaching the surface per unit time, then average drop diameters are approximately doubled (Markowitz, 1976) implying, from Figure 2, equilibration distances three to four times greater than the ones inferred above.

In conclusion, it appears that the accurate treatment of the washout of HTO requires that departures from equilibrium scavenging be taken into account, especially for small plume dimensions and low temperatures.

3.0 METHODS OF PARAMETERIZING PRECIPITATION SCAVENGING

Two simple methods are commonly used to parameterize precipitation scavenging, in order to model the effect of precipitation scavenging on (i) plume depletion and (2) concentrations of scavenged material in rainfall. These are the washout (or scavenging) coefficient and the washout (or scavenging) ratio. They are described below, and their relative merits discussed.

3.1 Washout Ratio

The washout ratio, w_r, is defined as the ratio of the concentration of scavenged material in rainfall, reaching the ground, to the concentration in the air at ground level ie,

$$c_l\ (z=0) = w_r\ c_g\ (z=0) \qquad (15)$$

The flux of scavenged material to the surface is thus given by

$$J = w_r\ R\ c_g\ (z=0) \qquad (16)$$

If the liquid phase concentrations are in equilibrium with the surrounding air then comparison of (2) with (15) shows that the corresponding "equilibrium" washout ratio is simply

$$w_{r_{eq}} = \alpha \qquad (17)$$

As discussed in Section 2.0, for equilibrium scavenging conditions to hold, vertical plume dimensions must be greater than typical drop equilibration distances. The use of the

equilibrium washout ratio will only be appropriate, therefore, at sufficiently large plume travel distances (corresponding to vertical plume dimensions of hundreds of meters or greater).

At shorter plume travel distances, where most drops do not spend sufficient time in the plume to equilibrate, rainfall concentrations may be expected to be significantly different from equilibrium values. For near ground level releases where maximum gas phase concentrations occur near ground level, equilibrium washout ratios will overestimate plume scavenging rates in the short range.

In the case of an elevated plume, the drops will scavenge tritium on passing through the plume. However, on reaching the air below the plume, they may retain liquid phase concentrations that are above equilibrium with the ambient air. The equilibrium washout ratio (which is referred to the gas phase concentration at ground level) may then underestimate concentrations in the rainfall reaching the ground. (Dana et al (1975) discuss this problem with regard to the washout of SO_2.)

3.2 Washout Coefficient

The washout coefficient, Λ is defined as the fraction of plume material scavenged per unit time. The treatment of plume depletion is thus particularly simple. A constant washout coefficient leads to an exponential decay of the effective source term, Q(x), with time, ie

$$Q(x) = Q(o) \exp(-\Lambda x/u) \qquad (18)$$

where Q(o) is the initial source term, u is the windspeed, and x is the plume travel distance (x/u is therefore the plume travel time).

The washout coefficient approach is most useful when the scavenging process can be considered irreversible, that is, when the term c_l/α in equation (4) can be neglected. The flux of material to the drop is thus simply

$$F = k_g c_g \qquad (19)$$

This condition holds when (i) the liquid phase concentrations are far less than the equilibrium values ($c_l \ll \alpha c_g$) or (ii) uptake is truly irreversible ($\alpha \to \infty$), for example, in the case of species that react on entering solution.

If the uptake of material to the drop is only limited by gas-phase mass transfer then the amount of material removed by a drop of diameter D is given by the product of the flux and the area. If there are n(D) drops of diameter D per unit volume per unit diameter, then the fraction of material removed per unit time is

$$\frac{1}{c_g}\frac{dc_g}{dt} = \Lambda = -\pi \int_0^\infty D^2 k_g n(D)\, dD \qquad (20)$$

Note that Λ depends only on the rain conditions (through n(D)) and the species diffusion coefficient (through k_g).

In order to calculate Λ a drop size distribution, n(D), is required. Many empirical fits to observed distributions are available, such as the Marshall Palmer distribution (Equation 11).

In the case of HTO, irreversible washout conditions would only be expected to hold at very short travel distances, where the plume vertical dimensions are much less than typical drop equilibration distances. At longer plume travel distances a washout coefficient, based on irreversible scavenging, may significantly overestimate plume depletion. The "true" washout coefficient for HTO will therefore be a parameter that is a function of downwind distance.

3.3 Relationship Between Washout Coefficient and Washout Ratio

For modelling purposes, the tendency is to characterize wet deposition by a parameter, that is independent of plume travel distance. It is apparent from our previous discussion that this is often not suitable for HTO, except at long enough travel distances for the washout ratio to approach the equilibrium value or at extremely short travel distances where most drops have not had time to equilibrate and where irreversible scavenging conditions would hold to a good approximation.

Before dealing with the problem of the dependence of w_r and Λ on downwind distance, we note that it is possible to relate these parameters by making the following assumptions: (i) raindrops fall vertically; (ii) plume steady-state conditions hold and (iii) scavenging does not significantly perturb the (normalized) vertical plume profile.

The fraction of material scavenged per unit time is then given by the flux of material reaching the ground divided by the amount of plume material above that point. Using (16) and the definition of washout coefficient we get

$$\Lambda = c_g(z = 0)\ Rw_r \left[\int_0^\infty c_g\, dz \right]^{-1} \tag{21}$$

which for a ground level release, and a Gaussian profile gives

$$\Lambda = \sqrt{2/\pi}\ \ Rw_r / \sigma_z \tag{22}$$

or expressing w_r in terms of Λ

$$w_r = \sqrt{\pi/2}\ \sigma_z\ \Lambda/R \tag{23}$$

Because of the dependence of this relationship on vertical plume dimensions it is only possible to have w_r and Λ both constant and independent of x if the vertical dimensions of the plume are constant. This may be a reasonable approximation at long travel distances where the plume is fully distributed through the mixing layer.

4.0 NON-EQUILIBRIUM WASHOUT RATIOS

As we have seen, an equilibrium washout approach may be suitable for treating the rain scavenging of HTO at sufficiently long travel distances. However, for shorter distances a significant fraction of the larger drops are not exposed to the plume for long enough periods to reach equilibrium. Hales (1972a, Hales et al 1973) has derived an analytic expression for the concentration of scavenged material, in a drop of radius D, that falls to the ground through a plume having a Gaussian profile. The derivation of this expression is outlined below. We then use this expression to derive non-equilibrium washout ratios.

The concentration distribution of a Gaussian plume, having a finite emission height h, is given by

$$c_g = \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}}\ \ \exp\left[-\frac{y^2}{2\sigma_y^2}\right]\ \left\{\exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right]\right. \tag{24}$$

where Q is the source term, corrected for depletion and σ_y and σ_z are the lateral and vertical standard deviations of the plume profile, respectively.

This expression can be substituted into the equation describing the rate of change of drop concentration in a drop of diameter D, falling with velocity, v_z, which is, from equation (7).

$$\frac{dc_\ell}{dz} = \frac{6\ k_g}{v_z D}\ (c_g - c_\ell/\alpha) \tag{25}$$

We assume a release from near ground level, or from a building where wake entrainment effects are likely to rapidly mix the plume to ground level. The vertical concentration distribution can thus be approximated by (24) with h=0. The drop is assumed neither to grow or evaporate on passage through the plume. This appears to be a reasonable assumption at ~100% RH (eg, Graedel and Goldberg, 1983).

Assuming also an initially uncontaminated drop, and vertical raindrop trajectories, (25) may be integrated over z to give the concentration, at ground level, in a drop of radius D.

$$c_\ell(D,\ z=0) = \frac{-Q}{\sqrt{2\pi}\ \sigma_y\ \bar{u}}\ \frac{6\ k_g}{v_z D}\ \exp\ [-y^2/2\sigma_y{}^2]$$

$$\exp\ [\tfrac{1}{2}\ (\sigma_z\ \frac{6\ k_g}{v_z D\alpha})^2]\ [1 - \mathrm{erf}\ (\frac{\sigma_z}{\sqrt{2}}\ \frac{6\ k_g}{v_z D\alpha})] \tag{26}$$

Note that v_z is negative as it represents a downward velocity. Hales (1972a, Hales et al 1973) also gives an expression for $c_\ell(D,\ z=0)$ for the case of a finite release height h. Only the simplified expression for h=0 is reproduced here.

At sufficiently long travel distances, where $\sigma_z \gg |v_z D\alpha/6k_g|$ $(= z_e)$, (25) can be written in the asymptotic form

$$c_\ell(D,z=0) = \frac{Q\alpha}{\pi\sigma_y\sigma_z\ \bar{u}}\ \exp\ [-\frac{y^2}{2\sigma_y{}^2}]\ [1 - (\frac{v_z D\alpha}{\sigma_z\ 6\ k_g})^2] \tag{27}$$

which can be written in terms of the equilibrium washout coefficient, $w_{r_{eq}} = \alpha$, and the equilibration distance, z_e, as

$$c_\ell(D,z=0) = c_g(z=0)\ w_{r_{eq}}[1 - (\frac{z_e}{\sigma_z})^2] \tag{28}$$

Assuming steady-state conditions, and an unchanging plume profile, the flux of scavenged material to the ground can be obtained by integrating the product of concentration, drop volume and fall velocity over the drop size distribution.

$$J = \frac{\pi}{6} \int_0^\infty D^3 \, v_z \, (D) \, n \, (D) \, c_\ell \, (D, z=0) \, dD \qquad (29)$$

This may be used to calculate the (effective) washout ratio and (effective) washout coefficient using (16) and (21), ie,

$$w_r = J \, [c_g(z=0) \, R]^{-1} \qquad (30)$$

and

$$\Lambda = J \, [\int c_g(z) \, dz]^{-1}$$

$$= J \, [\sigma_z \sqrt{\pi/2} \;\; c_g(z=0)]^{-1} \qquad (31)$$

Equations (26) and (29) were substituted in (30) and the integral evaluated numerically using Simpson's rule. The asymptotic form (27) was used where appropriate to avoid computer overflow and underflow problems. Note that w_r and Λ do not depend on crosswind distance as the y dependence cancels. The Marshall-Palmer drop-size distribution (11) was used together with data from Tables I and II.

Practical lower and upper limits for the integration were chosen as $D_{min} = 0.02$ cm and $D_{max} = 0.6$ cm, respectively. By comparison with observed drop size distributions (eg, Markowitz, 1976) these limits would include >95% of the rainfall. The difficulty of choosing an appropriate lower cut-off diameter, for calculations of this kind, has been discussed in detail by Levine and Schwartz (1982). They conclude that 0.02 cm is a reasonable dividing line between cloud and raindrops, and hence is a reasonable minimum diameter for the consideration of below cloud scavenging. They also point out that the Marshall-Palmer distribution may overestimate the number of drops in the range $0.02 < D < 0.12$ cm by about 50%. The sensitivity of the washout ratios, derived here, to D_{min} is examined later.

Another point of some practical importance is to note that the rainfall rate, R, appearing as a parameter in the drop size distribution, is usually not consistent with R derived as the flux of water to the ground predicted by n(D) and v_z, (eg, Markowitz, 1976; Bennet et al, 1984; Fenton et al, 1980), ie,

$$R = \frac{\pi}{6} \int_0^\infty D^3 \, n(D) \, v_z(D) \, dD. \qquad (32)$$

Consequently, to be consistent with the use of (29) to determine J, (32) was also numerically evaluated, using similar integration limits, and used in (30) to determine w_r.

Figure 4 shows plots of w_r, for HTO, calculated for various temperatures, rainfall rates (ranging from light to very heavy rainfall) and σ_z values. As expected, at long travel distances $w_r \to w_{r_{eq}}$, where $w_{r_{eq}}$ is the equilibrium washout ratio, equal to α (Table I). Equilibrium is also more rapidly achieved at higher temperatures (as equilibrium washout ratios are lower, less material needs to be transported to the drop to reach equilibrium) and at lower rainfall rates (fewer large drops which take longer to equilibrate).

For practical purposes, the following empirical expression was found to provide a reasonable fit to w_r.

$$\frac{w_r}{w_{r_{eq}}} = 1 - \exp[-f(\sigma_z, T, R)] \qquad (33)$$

where

$$f(\sigma_z, T, R) = 6.3 \times 10^{-3} \, R^{-0.35} \sigma_z^{0.8} \exp[4.3(3.66 - 10^3/T)]$$

where σ_z is expressed in m, R in mm h^{-1} and T in degrees Kelvin and $w_{r_{eq}} = \alpha$ from Table I. This expression generally agrees within 10% with the numerically calculated values shown in Figure 4, except at low T, high R and small σ_z. (However, even in the worst case, T = 0°C, σ_z = 10 m and R = 25 mm h^{-1}, results are still within a factor of two). Given the uncertainties involved in the calculation of w_r, and indeed the inherent variability in the washout process itself (rainfall rates may vary greatly both with position and time), this expression should provide a satisfactory fit for practical estimates of washout.

The functional form of (33) was chosen as it had the correct limiting behaviour as $\sigma_z \to 0$ and $\sigma_z \to \infty$. The temperature dependence of the coefficient f was found to be well described by a form similar to that of the temperature dependence of vapour pressure (eg, Metz 1976). The dependence of f on σ_z and R was reasonably well fitted by power laws.

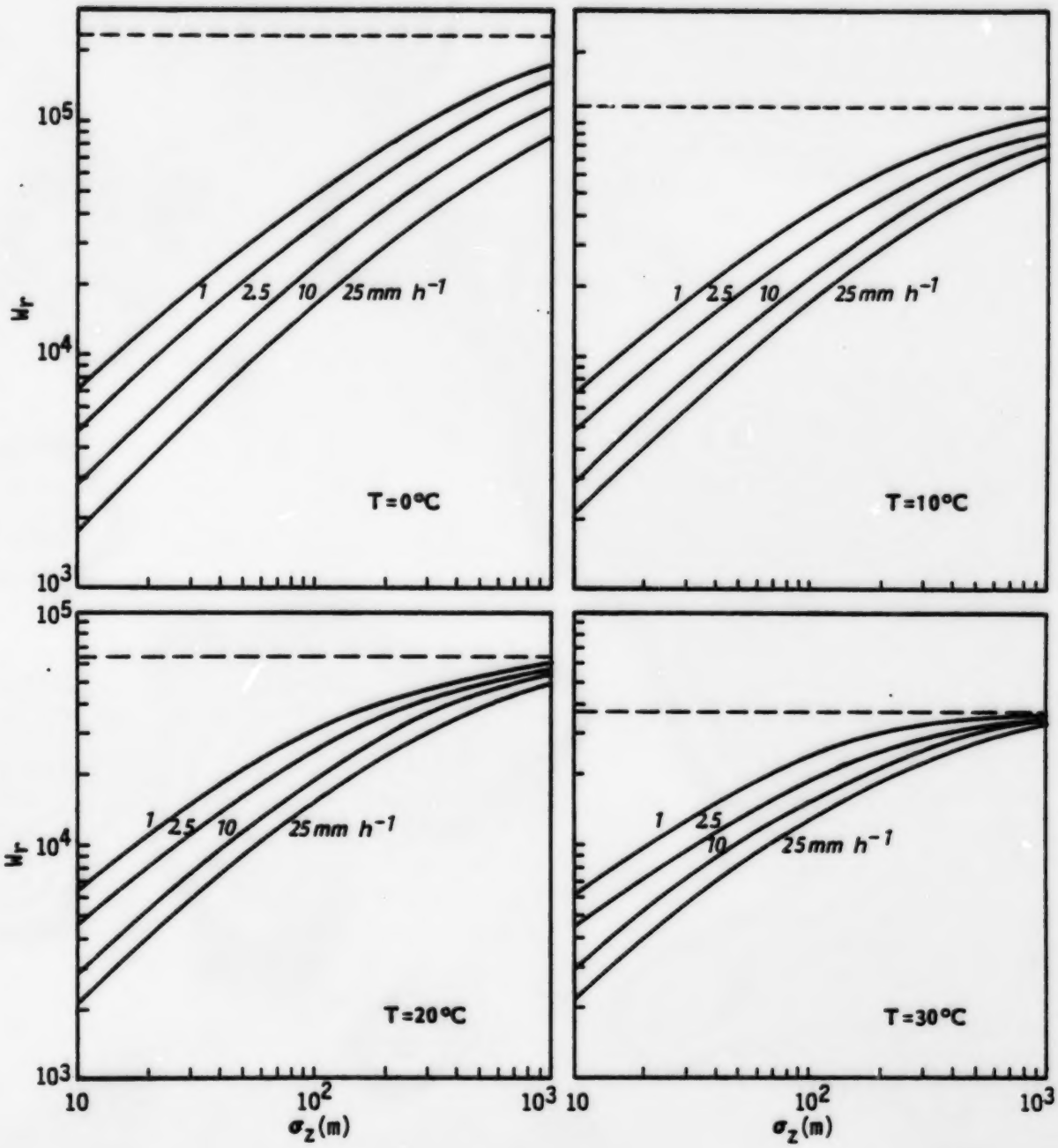

FIGURE 4

HTO WASHOUT RATIOS CALCULATED FOR VARIOUS TEMPERATURES AND RAINFALL RATES AS A FUNCTION OF PLUME VERTICAL STANDARD DEVIATION, σ_z. THE DASHED LINES SHOW, FOR EACH TEMPERATURE, THE EQUILIBRIUM WASHOUT RATIO APPROACHED ASYMPTOTICALLY AS σ_z INCREASES.

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The sensitivity of numerically calculated nonequilibrium washout ratios to various factors was examined and is described below.

Effect of drop size limits on w_r

As briefly discussed earlier, Levine and Schwartz (1982), in a study of the washout of HNO_3 have pointed out that irreversible scavenging coefficients calculated using an expression similar to (20) are quite sensitive to the lower limit chosen for drop diameter, D_{min}. In the case of irreversible scavenging this is very important as small drops tend to scavenge material most rapidly. However, in the case of the above calculations for HTO, derived washout ratios will probably be less sensitive to D_{min} as small drops (i) will equilibrate rapidly and (ii) make up a small fraction of the total mass flux. This was verified by determining the sensitivity of derived washout ratios, to D_{min}, for two extreme cases: (i) low σ_z (10 m) and T (0°C), where most of the drops would be expected to be far from equilibrium, and hence near irreversible scavenging conditions would be expected to hold; and (ii) large σ_z (1000 m) and high T (30°C), where near equilibrium conditions would be expected to hold. An input rainfall rate of 2.5 mm h^{-1} was used.

Table III shows the results. Note that the value of R, used in equation (30), was determined in each case using the corresponding D_{min}, and also depends significantly on D_{min}. In the worst case (lowest T, smallest σ_z) the variation of D_{min} from 0.02 cm to 0.12 cm introduced a factor of ~3 change in w_r. Under near equilibrium conditions, however, (high T, large σ_z) w_r did not change significantly with D_{min}.

Increasing the upper limit, of the integral, to values of $D_{max} > 0.6$ cm did not affect the results significantly, reflecting the fact that the Marshall-Palmer distribution predicts very few drops of greater diameter.

TABLE III
Sensitivity of derived washout ratios to minimum drop diameter (for a rainfall rate of 2.5 mm h^{-1})

D_{min} (cm)	R_{input}[a] (mm h^{-1})	R_{calc}[b] (mm h^{-1})	w_r	
			T=0°, σ_z=10 m	T=30°C, σ_z=1000 m
0	2.5	3.33	4.7×10^3	3.5×10^4
0.02	"	3.14	3.3×10^3	3.5×10^4
0.06	"	2.71	2.1×10^3	3.5×10^4
0.12	"	1.55	1.7×10^3	3.4×10^4

a - Input parameter to Marshal-Palmer distribution
b - Calculated from (32) and used in expression (30) for w_r

Effect of raindrop size distribution and fall velocity on w_r

Numerous empirical formulas are available for describing drop size distributions and drop fall velocities. The sensitivity of derived washout ratios to choice of formula was investigated for two conditions. The first with T=0°C, R=2.5 mm h^{-1} and σ_z = 10 m represents a case with most drops far from equilibrium. For comparison an intermediate case of T=10°C, R=2.5 mm h^{-1} and σ_z=100 m was also treated. For near equilibrium washout conditions, the washout ratio is expected to become independent of drop size distribution and fall velocity.

Results are shown in Table IV. In addition to the Marshall-Palmer (1971) distribution (11), the Sekhorn-Srivastava (1971) distribution given below was used.

$$n(D) = 0.07\ R^{0.37}\ \exp[-38\ D\ R^{-0.14}]\ cm^{-4}$$

The terminal velocity formulas used were those due to Kessler (1969), given in Table II, and Best (1980) as follows,

$$v_z = 958\ (1 - \exp\ (-(D/0.177)^{1.147})\ cm\ s^{-1}$$

and Hales et al (1973) as follows,

$$v_z = 4355.5\ D - 4507.4\ D^2 - 4023.1\ D^3\ cm\ s^{-1}$$

where D is in cm.

Note that the derived rainfall rate (32) again depends on drop-size distribution and velocity formula, and was calculated in each case.

It can be seen that calculated w_r values are very insensitive to the choice of drop-size distribution and velocity formula.

TABLE IV

HTO Washout ratios calculated for various drop size distributions and drop terminal velocity formulas.

$T=0°C$, $\sigma_z=10$ m, $R=2.5$ mm h^{-1}

v_z Formula → / Drop size distribution ↓	Kessler (1969)	Best (1950)	Hales et al (1973)
Marshall-Palmer	4.68×10^3	4.64×10^3	4.54×10^3
Sekhorn-Srivastava	4.58×10^3	--	--

$T=10°C$, $\sigma_z=100$ m, $R=2.5$ mm h^{-1}

v_z Formula → / Drop size distribution ↓	Kessler (1969)	Best (1950)	Hales et al (1973)
Marshall-Palmer	3.12×10^4	3.16×10^4	3.12×10^4
Sekhorn-Srivastava	3.09×10^4	--	--

4.1 Non-Equilibrium Washout Coefficients

If desired, effective washout coefficients may be obtained from the washout ratios derived in the previous section by using (22). As an example, derived washout coefficients for T=10°C and various (input) rainfall rates are shown in Figure 5. At small σ_z, Λ tends towards the asymptotic value corresponding to the irreversible scavenging coefficient given by (19), as expected because most drops would not have attained equilibrium. At long travel distance (large σ_z) Λ tends towards the equilibrium scavenging coefficient given by,

$$\Lambda_{eq} = \sqrt{2/\pi}\, w_{r_{eq}}\, R/\sigma_z \qquad (34)$$

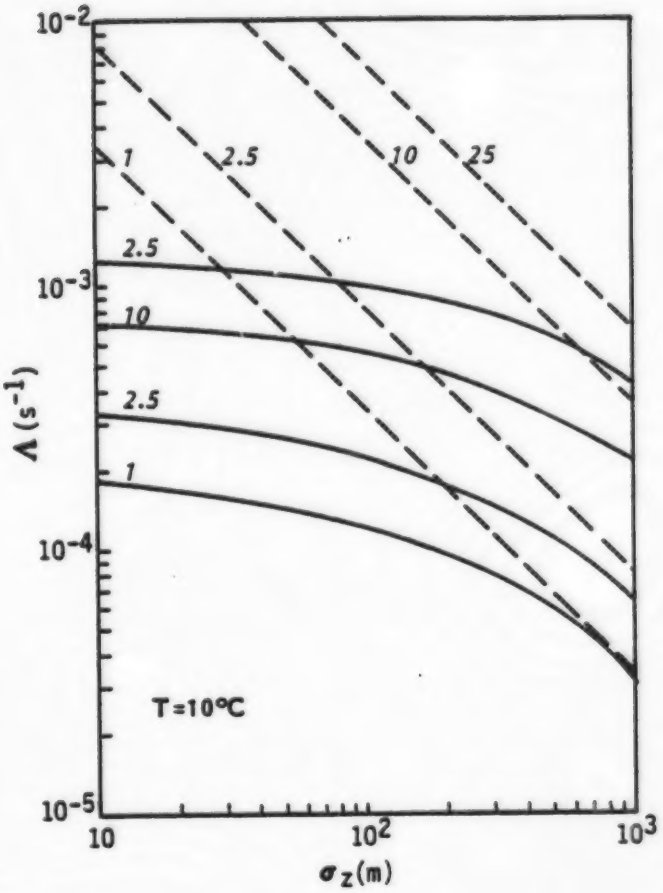

FIGURE 5

EFFECTIVE HTO WASHOUT COEFFICIENT PLOTTED AGAINST PLUME VERTICAL STANDARD DEVIATION, FOR VARIOUS RAINFALL RATES (mm h^{-1}) AT T=10°C. THE DASHED LINES INDICATE THE CORRESPONDING EQUILIBRIUM WASH-OUT COEFFICIENTS.

Equilibrium scavenging coefficients for the various rainfall rates are shown by dashed lines. This figure dramatically illustrates how the use of equilibrium scavenging coefficients at short travel distances may greatly overestimate washout.

5.0 DEPLETION OF A HTO PLUME BY WASHOUT

Equation (33), which gives the HTO washout ratio, taking into account deviations from equilibrium, can be used to estimate the degree of depletion of a HTO plume caused by washout. Noting that the flux of plume material to the ground is

$$J = w_r \, R \, c_g \quad (z=0) \tag{35}$$

an effective wet deposition velocity (ratio of flux to ground level concentration) can be defined in a similar way to dry deposition velocity as (Slinn 1984)

$$v_w = w_r \, R. \tag{36}$$

At a rainfall rate of 2.5 mm h^{-1}, v_w's corresponding to equilibrium washout range from 16.3 to 2.5 cm s^{-1} for T ranging from 0°C to 30°C. In comparison, dry deposition velocities for HTO are ~1 cm s^{-1} (Garland 1979).

The effect of washout can thus be treated in a similar way to dry deposition. The simplest method is to calculate an effective source term Q(x), appropriately modified to account for depletion by washout (Chamberlain 1953, Van der Hoven 1968). Assuming that the (normalized) plume profile is not affected by the deposition process and is of Gaussian form, it can be shown that the ratio of Q(x) to Q(o), the initial source term, is

$$\frac{Q(x)}{Q(o)} = \exp\left[-\left(\frac{2}{\pi}\right)^{1/2} \frac{1}{u} \int_o^x \frac{v_w}{\sigma_z \exp\left(\frac{h^2}{2\sigma_z^2}\right)} \, dx'\right] \tag{37}$$

which for constant σ_z and v_g leads to an exponentially decaying Q(x). In practice, the vertical dimensions of a plume will grow until the plume is fully mixed throughout the mixing layer. v_w is also dependent on σ_z.

Using expression (33) for w_r, (37) was integrated numerically. (Because w_r does not depend on y, v_w depends only on x). Figure 6 shows values of $Q(x)/Q(o)$ and of the fractional amount of plume material deposited, $F(x) = 1 - Q(x)/Q(o)$, plotted against plume travel distance, for various temperatures, a rainfall rate of 2.5 mm h^{-1}, a wind speed of 5 ms^{-1} and stability class D (corresponding to neutral stability conditions, which are likely to prevail under conditions of rain). The formula developed by Smith (1972) and Hosker (1974) was used to evaluate σ_z, assuming a surface roughness length of 40 cm (typical of the outskirts of towns).

As expected, the degree of depletion increases with decreasing temperature because of the increasing equilibrium washout ratio. However, the degree of depletion is not as sensitive to temperature as the equilibrium washout ratio. This is particularly true at short travel distances, where many of the drops are far from equilibrium, and thus scavenge material in an irreversible way, the rate of which is not strongly temperature dependent.

To illustrate how poor the assumption of equilibrium washout may be for short travel distances, equation (37) was evaluated using $v_w = \text{const} = w_{r_{eq}} R$, for T = 10°C. The results are shown as the dotted lines in Figure 6. The extent of plume depletion is far greater, indicating that large errors may be incurred by the inappropriate use of equilibrium scavenging coefficients. The error is less at higher temperatures where the washout ratio is smaller, and equilibrium is reached more rapidly.

6.0 SCAVENGING OF HTO BY SNOW

Little theoretical or experimental information is available regarding the scavenging of HTO by snow.

If it is assumed that HTO is absorbed or exchanged at the surface of the snow crystal in an irreversible way, then HTO snowout can be treated similarly to other irreversibly scavenged gases such as HNO_3. This approach should at least give an approximate upper limit on the HTO snow-scavenging coefficient.

The treatment developed by Chang (1984), to describe "snowout" of HNO_3, was thus adapted for HTO by taking into account the difference in diffusion coefficients of the two species. The approach is similar to that for treating irreversible scavenging by rain (20) and involves integrating an expression for the rate of uptake by a snow particle, of particular dimensions, over a snow particle size distribution. For HTO this can be shown to give (using data from Table II) the following expression for the snow-scavenging or snowout coefficient, Λ_s, (which is analogous to the washout coefficient discussed previously).

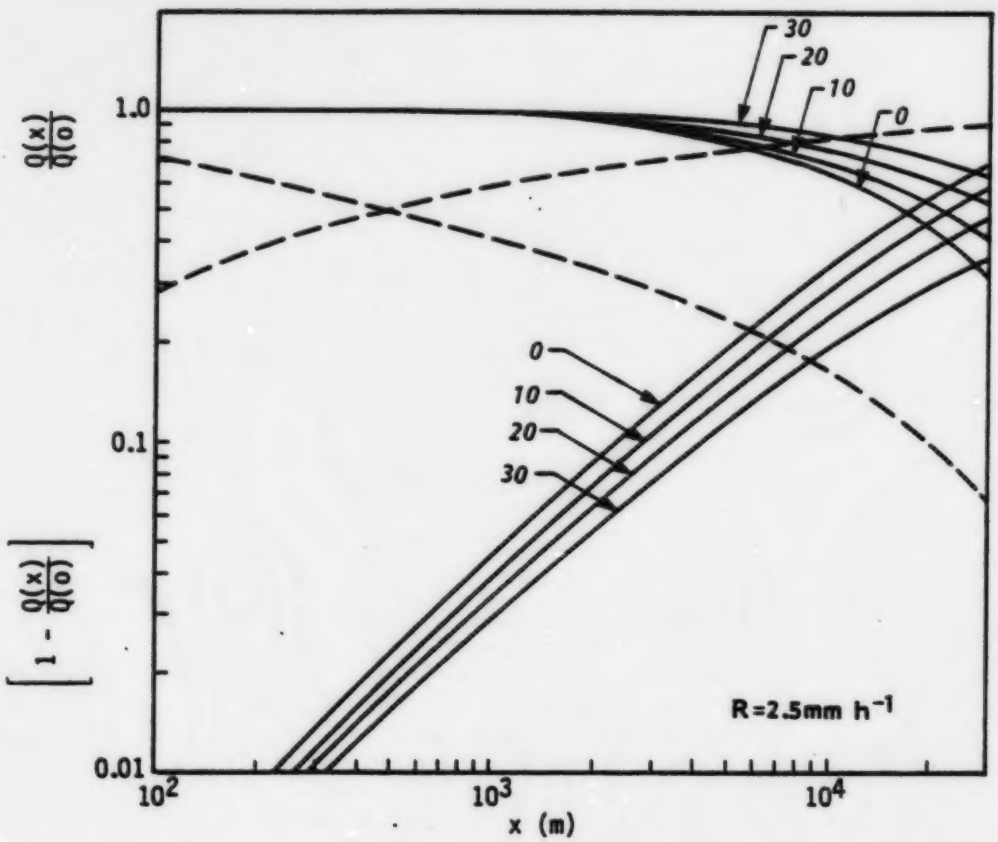

FIGURE 6

SOURCE TERM DEPLETION, AND FRACTION OF PLUME MATERIAL WASHED OUT, PLOTTED AGAINST TRAVEL DISTANCE, FOR VARIOUS TEMPERATURES (INDICATED), A WIND SPEED OF 5 ms^{-1}, STABILITY CLASS D AND A RAINFALL RATE OF 2.5 mm h^{-1}. THE DASHED LINES SHOW VALUES CALCULATED ASSUMING EQUILIBRIUM SCAVENGING.

$$\Lambda_s = 1.2 \times 10^{-4} R^{0.33} + 3.0 \times 10^{-4} R^{0.64} \ s^{-1} \quad (38)$$

where R is the precipitation rate in mm h^{-1} equivalent water.

Values of Λ_s calculated from (38) for a range of precipitation rates are given in Table V.

TABLE V

HTO Snow-scavenging Coefficients

R(mm h^{-1})	0.1	0.5	1	2
Λ_s (s^{-1})	2.0×10^{-4}	2.9×10^{-4}	4.2×10^{-4}	6.1×10^{-4}

7.0 DISCUSSION

It is clear that it is not possible to parameterize HTO washout in terms of a simple washout coefficient or ratio that is independent of plume travel distance, except at long enough distances for equilibrium scavenging conditions to hold. In the latter case the equilibrium washout ratio is given by the equilibrium ratio between liquid and gas phase HTO concentrations, α, which is dependent on temperature alone (Table 1).

It is also apparent that transport models, used to assess the fate and impact of HTO releases, which are based on equilibrium scavenging assumptions, such as that of Bander et al (1979) and the Ontario Hydro Tritium Dispersion Code (CFFTP 1984), will greatly overestimate plume depletion and rainfall HTO concentrations in the short range.

Consequently, a formula for washout ratio has been developed which describes the degree of departure of rainfall concentrations from equilibrium, in terms of the vertical dimensions of the plume and temperature, for a plume that emanates from near ground level.

Equivalent effective scavenging coefficients may be calculated from the washout ratio; however, the washout ratio approach is preferred for treating the rain scavenging of HTO, as HTO may be treated as a gas of "finite solubility" and w_r is much less sensitive to rainfall rate. In contrast, a scavenging coefficient approach is more appropriate for the treatment of snow scavenging, as the uptake is likely to be essentially irreversible.

Unfortunately, very little data exist for validation of these theoretical predictions. Calculated washout ratios should therefore be used with caution, except, perhaps at long travel distances where it is reasonable to assume that equilibrium scavenging conditions hold. Dana et al (1978) describe a rain scavenging experiment involving an elevated release of HTO (with a 60 m release height and sampling of rainfall along two arcs at 400 m and 800 m travel distance, respectively). Because of the elevated nature of the plume the results cannot be directly compared to the present theory.

It would be desirable, therefore, to test the present theory by field measurements. Washout ratios (being the ratio of concentrations of HTO in precipitation and air at ground level) should be relatively straightforward to measure using routine emissions. Measurements of w_r for a variety of travel distances, precipitation rates, temperatures and wind speeds would give an idea of the statistical dependence of w_r on these parameters. Under conditions of rain, the atmospheric stability is likely to be near neutral, σ_z would therefore be determined mainly by the plume travel distance x. The dependence of w_r on σ_z should therefore be apparent as a dependence on x.

Finally, the possible importance of factors not treated in the present analysis is briefly discussed.

(1) Release Height

The treatment could be modified to include an elevated plume and the corresponding HTO uptake to and possibly remission from falling drops. However, it is felt that there is little point in doing this for Ontario Hydro's CANDU type stations where releases are unlikely to be significantly greater than building height. Building wake effects are likely to rapidly mix the plume to ground level, the situation can therefore be treated to a good approximation as a ground level release with plume vertical dimensions increased by an amount related to the building height (eg, Huber 1984).

(2) Cloud-Plume Interaction

If the plume is mixed vertically into the region where rain drops form, then the assumptions of the present treatment no longer hold. Mixing of the plume into the cloud may allow drops to form with initial HTO concentrations that are near equilibrium. Cloud-plume mixing is however only likely to occur at long travel distances, where near equilibrium scavenging conditions are expected to hold, irrespective of the mixing of the plume into clouds. Fog droplets would be likely to equilibrate with the ambient air, because of their relatively long residence time.

(3) Effect of washout on plume distribution

As pointed out earlier, because smaller drops are likely to reach equilibrium more rapidly, the upper levels of the plume will be depleted more rapidly, than lower levels. This may lead to some distortion of the plume profile.

(4) Exchange of HTO between fallen rain and air

Even though the rain reaching the ground may not be in equilibrium with the air concentration, fallen rain lying on the surface will tend to equilibrate with the air above it, through exchange, either perhaps increasing the liquid phase HTO concentration if the plume remains above that point, or decreasing it if the plume moves away (because of change in wind direction).

An order of magnitude estimate of equilibration times for fallen rain can be obtained by assuming that the exchange is gas phase controlled. Assuming a constant gas phase concentration it is straightforward to show (eg, Horton et al, 1971) that the equilibration time for the liquid phase concentration is

$$\tau = \alpha z / k_g$$

where z is the depth of water and k_g is an effective gas phase transfer velocity. Taking α from Table I, z=1 mm and k_g=1 cm s^{-1} values of τ range from ~6.5 h for T=0°C to ~1 h for T=30°C. (An exchange velocity of k_g ~0.3 cm s^{-1} can be inferred from the laboratory experiments of Horton et al (1971) carried out at T=24.5°C, indicating that the above values may underestimate τ.)

8.0 CONCLUSIONS

Potential methods of treating the precipitation scavenging of HTO were investigated. It was suggested that the use of a washout ratio was most suitable for treating the rain scavenging of HTO. It was shown that the assumption of equilibrium scavenging is likely to greatly overestimate plume depletion, especially at short plume travel distances. Washout ratios or coefficients based on the equilibrium assumption should not be used under these conditions. An empirical expression for the non-equilibrium washout ratio as a function of temperature and plume dimensions was therefore derived. An upper limit to the scavenging coefficient for snow was estimated by assuming irreversible, gas phase transfer limited uptake. A scavenging coefficient approach is most suitable for treating irreversible uptake.

It was pointed out that very little experimental information exists to validate these treatments. Derived washout parameters should therefore be used with caution until verified by field measurements.

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